

EFFECT OF TiO_2 AS AN ADDITIVE ON THE PHASE FORMATION AND DENSIFICATION OF MULLITE-ZIRCONIA COMPOSITES

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENT FOR THE DEGREE OF
BACHELOR OF TECHNOLOGY

by
VINI BHAGAT
ROLL NO. 10608008



DEPARTMENT OF CERAMIC ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY ROURLKELA
2009-2010



NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA

2010

CERTIFICATE

This is to certify that the thesis entitled, **“Effect of TiO_2 as an additive on the phase formation and densification of mullite-zirconia composites”** submitted by **Miss Vini Bhagat** in partial fulfillment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.

S.K.PRATIHAR

PROFESSOR

Department of Ceramic Engineering

National Institute of Technology

Date: 7.05.2010

Rourkela-769008

ACKNOWLEDGEMENT

I express my deep gratitude to my guide, Prof S.K. Pratihara for his valuable advice, time and guidance in the completion of this project work. My heartfelt thanks to all the faculty members for their suggestions during this project work. My sincere acknowledgement to the Research Scholars, M. Tech students and the non-teaching staff for the help and cooperation extended to us. And finally, my hearty thanks to all my friends who have constantly helped me.

Vini Bhagat

10608008

ABSTRACT

Mullite-Zirconia composite was prepared from reaction sintering of zircon sand and alumina with different percentages of titanium dioxide. The mixture was uniaxially compacted and sintered at 1500°C, 1550°C and 1650°C with 4hrs. soaking time. The density, biaxial flexure strength and XRD were carried out on different sintered samples. Maximum density and approximate zero porosity was achieved at 1600°C in sample containing 0.2% TiO₂. Addition of additive increased the biaxial flexural strength of the zirconia-mullite composites.

CONTENTS

CERTIFICATE

ACKNOWLEDGEMENTS

ABSTRACT

CHAPTER 1 : GENERAL INTRODUCTION	6
1.1 Introduction	6
1.2 Occurence	7
1.3 Different polymorphs of zirconia	7
1.4 Phase transformations	7
1.5 Unstabilized, stabilized and partially stabilized zirconia	8
1.6 Mullite.....	9
1.7 Mullite-Zirconia composites	11
CHAPTER 2~ LITERATURE REVIEW	13
2.1 Effect of additives on the properties of Zirconia- Mullite composites.....	13
2.2 Objective of the present study.....	15
CHAPTER 3~ EXPERIMENTAL PROCEDURE.....	16
3.1 Procedure.....	16
3.2 General Characterization	18
CHAPTER 4 ~ RESULTS AND DISCUSSIONS	20
4.1 Densification Study	20
4.2 Change in linear dimensions	23
4.3 Biaxial flexural strength	26
4.4PhaseAnalysis.....	28
CHAPTER 5~ CONCLUSION	31
REFERENCES	32

CHAPTER 1

GENERAL INTRODUCTION

1.1 INTRODUCTION

Zircon has been known as a gem from ancient times Zirconium oxide is one of the most studied materials in the aspects of mechanical, structural and electrical properties. It has high melting point($\sim 2700^{\circ}\text{C}$) and is well known for good wear resistance, hardness, low coefficient of friction, chemical inertness, elastic modulus ionic conductivity, low thermal conductivity and high melting temperature that make it useful in zirconia ceramics from the structural point of view. In addition, they are applied in electrochemical cells (fuel cells, oxygen sensors, oxygen pumps, etc.) due to their high oxygen-ion conductivity at elevated temperatures. Although low-quality zirconia is used as an abrasive in huge quantities, tough, wear resistant, refractory zirconia ceramics are used to manufacture parts operating in aggressive environments, like extrusion dies, valves and port liners for combustion engines, low corrosion, thermal shock resistant refractory liners or valve parts in foundries. Zirconia blades are used to cut Kevlar, magnetic tapes, cigarette filters (because of their reduced wear). Good chemical and dimensional stability, mechanical strength and toughness, coupled with a Young's modulus in the same order of magnitude of stainless steel alloys was the origin of the interest in using zirconia as a ceramic biomaterial. In addition, they are applied in electrochemical cells (fuel cells, oxygen sensors, oxygen pumps, etc.) due to their high oxygen-ion conductivity at elevated temperatures.

1.2 OCCURRENCE

Zirconium is found in two minerals, zircon (zirconium silicate, ZrSiO_4) and baddeleyite (zirconium oxide, ZrO_2). The most important of these ores, zircon, occurs as grains concentrated in sand deposits in Kerala, Florida and South Africa. The sands are called zircon sands because they contain sand-sized mineral zircon grains. Most heavy-mineral sands also have a high content of titanium -bearing minerals, such as ilmenite and rutile.

1.3 DIFFERENT POLYMORPHS OF ZIRCONIA

The ZrO_2 exists in three polymorphs: cubic (c), tetragonal (t) and monoclinic (m). The stable form of zirconia at room temperature ($\sim 25^\circ\text{C}$) is monoclinic. As we increase the temperature, more symmetric crystal structures become stable. At 1170°C , the monoclinic zirconia transforms into a tetragonal structure. The tetragonal structure is stable up to 2370°C . At that temperature, zirconia transforms into a cubic form. The cubic form remains stable from 2370°C to a melting temperature of 2680°C .

1.4 PHASE TRANSFORMATIONS

The monoclinic/tetragonal transformation in zirconia is thermodynamically reversible but associated with large volume change (3 to 5%).i.e. contraction on heating and expansion on cooling. On cooling the $t \longrightarrow m$ transformation occurs at 900°C and is accompanied by the directional 5 % increase in volume. This transformation monoclinic to tetragonal or vice versa is also termed as martensitic transformation. This martensic phase transformation of zirconia when used in composites, under applied stress contributes considerably to the mechanical properties of ceramics. Zirconia can also have orthorhombic form, when high pressures are applied.

1.5 UNSTABILIZED, STABILIZED AND PARTIALLY STABILIZED ZIRCONIA

Commercial zirconia grades are usually unstabilized zirconia (i.e., fully monoclinic), partially stabilized zirconia, and stabilized zirconia (i.e., completely cubic) grades that exist commercially and are available among advanced ceramic producers worldwide. They are briefly described as follows:

- (i) Unstabilized zirconia – Pure zirconia is monoclinic at room temperature and changes to the denser tetragonal form at 1100°C, which involves a large volume change and creates micro cracks within its structure. Pure zirconia can be used as an additive to enhance the properties of other oxide refractories. It is particularly advantageous when added to high fired magnesia and alumina bodies as it promotes sinterability and with alumina contributes to abrasive characteristics.
- (ii) Partially stabilized zirconia- It is a mixture of various zirconia polymorphs, because insufficient cubic phase forming oxide has been added and a cubic plus metastable tetragonal ZrO_2 mixture is obtained. A smaller addition of stabilizer to zirconia will bring its structure into a tetragonal phase at a temperature higher than 1100°C, and a mixture of cubic phase and monoclinic or tetragonal phase at a lower temperature. Therefore partially stabilized zirconia is also called *tetragonal zirconia polycrystal (TZP)*, which is generally a zirconia doped with 2-3mol% of yttria that exhibits most impressive mechanical properties at room temperature.
- (iii) Fully stabilized zirconia- It is also called cubic stabilized zirconia and is essentially a single phase cubic material with large grain sizes that result when the stabilizer content and sintering temperatures place it entirely in the cubic phase region. Generally the addition of 16 mol% CaO, 16mol% MgO or 8mol% Y_2O_3 to a zirconia

structure is needed to form a fully stabilized zirconia. Its structure becomes cubic solid solution, which has no phase transformation from room temperature up to 2710°C.⁽¹⁾

1.6 MULLITE

Mullite is an alumino- silicate widely used in traditional refractory applications and one of the most studied crystalline phases in $\text{Al}_2\text{O}_3\text{-SiO}_2$ system. Mullite has achieved outstanding importance as a material for both traditional and advanced ceramics. Due to its high temperature but low pressure formation conditions, mullite occurs very rarely in nature. It has been found at the contact of superheated magma intrusions with Al_2O_3 -rich sediments, as on the Island of Mull (Scotland), where the name mullite comes from.

Mullite has many advantageous properties for refractory materials: (1) high melting point; (2) little deformation under load due to good creep resistance; (3) low thermal expansion , which yields good thermal shock resistance; (4) high shear modulus; and (5) good corrosion resistance. Taking advantage of these favorable characteristics, mullite based materials can be used as refractories in many industrial fields. The steel- making industry is the largest market for refractories and mullite based bricks are used for the lining in various furnaces. Mullite based bricks are the main constituents of the lining of the upper parts of melting furnaces, hot blast stoves, hot iron runners, and continuous casting furnaces.

Various types of mullites, depending on their synthesis procedures have been described as being relevant for ceramics:

- Sinter-mullites, produced by heat treatment of the starting materials, essentially via solid-state reactions. These mullites tend to have “stoichiometric”, i.e., 3/2-composition ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, i.e., $\approx 72 \text{ wt } \% \text{ Al}_2\text{O}_3$, $x = 0.25$).
- Fused –mullites, produced by crystallizing of alumino silicate melts. These mullite tend to be Al_2O_3 –rich with approximate 2/1 composition ($2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, i.e., $\approx 78 \text{ wt.} \% \text{ Al}_2\text{O}_3$, $x = 0.40$).
- Chemical-mullites, produced by heat treatment of organic or inorganic precursors. The composition of such mullites strongly depends on the starting materials and the temperature treatment. Extremely Al_2O_3 -rich compounds ($>90 \text{ wt} \% \text{ Al}_2\text{O}_3$, $x > 0.80$) have been identified at synthesis temperatures $<1000 \text{ }^\circ\text{C}$.

Reaction sintering of Al_2O_3 and SiO_2 bearing materials is a low cost method of mullite formation. The temperature and rate of mullite formation depends on the starting material, particularly on the Al_2O_3 and SiO_2 reactants used, their chemical purity and particle size distribution. The common SiO_2 and Al_2O_3 containing reactants used are Al_2O_3 and SiO_2 powder, refractory grade bauxite, clay and gibbsite.

For most applications, mullite is synthetically made following various routes, with predominance of reaction sintering from alumina and silica precursors. The stable composition range of mullite in the Al_2O_3 – SiO_2 system is $\cong 70.5$ – $74 \text{ wt.} \% \text{ Al}_2\text{O}_3^{(2)}$, and its theoretical density varies between 3160 and 3220 kg/m^3 . The stoichiometric mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ corresponds to $71.8 \text{ wt} \%$ alumina. The performance of refractory materials based on mullite, is governed by chemical composition, which usually contain 47 – $70 \text{ wt.} \% \text{ Al}_2\text{O}_3$ and by the sintered microstructure. Fused mullite or sintered mullite with low grain boundary populations and

relatively large size ($>40\text{ }\mu\text{m}$) equi-axed grains are preferred for refractory applications due to their relatively high resistance to attack by the slag ⁽³⁾. The morphology of mullite grains derived from silica-rich compositions is needle-like, whereas that from alumina-rich compositions is more equi-axed. The evolution of mullite microstructure is not only influenced by the chemical composition but also by the nature of the starting raw materials ⁽⁴⁾.

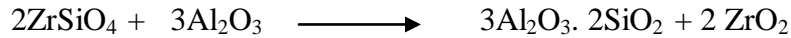
Reaction sintering of Al_2O_3 and SiO_2 bearing materials is a low cost method of mullite formation. The temperature and rate of mullite formation depends on the starting material, particularly on the Al_2O_3 and SiO_2 reactants used their chemical purity and particle size distribution. The common SiO_2 and Al_2O_3 containing reactants used are Al_2O_3 and SiO_2 powder, refractory grade bauxite, clay and gibbsite.

1.7 MULLITE- ZIRCONIA COMPOSITES

Mullite zirconia composites are materials with important technological applications due to their good properties such as toughness, chemical stability, and high-creep resistance. Mullite is an alumino-silicate widely used in traditional refractory application. Its good chemical inertness, low thermal conductivity, high creep resistance, low thermal expansion coefficient make it suitable for high temperature application use but relatively poor mechanical properties and difficulty in sintering has prevented its wide spread application. One of the ways to improve the sintering and mechanical properties of mullite is by zirconia addition. In solid solution ZrO_2 increases the sintering rate of mullite and as a second phase, acts as a grain growth inhibitor and transformation toughening agent.

The extensive use of mullite- zirconia composites is due to the fact that the zirconia dispersion in mullite matrix improves the thermo-mechanical properties leading to toughness by

transformation and micro cracking. Particularly in refractories, mullite and zirconia are both phases resulting from the use of zircon and alumina. Zircon (ZrSiO_4) acts as a bonding phase and its thermal decomposition adds zirconia and silica to the material.



The starting decomposition temperature of zircon is about 1675°C according to the $\text{ZrO}_2\text{--SiO}_2$ phase diagram ^[5]. The existence of some impurities in the starting powder can be lowered the decomposition temperature conspicuously ^[6]. During reaction bonding, the zircon dissociation and mullite formation commence at $\sim 1400^\circ\text{C}$ and are practically completed by 1500°C ^[7]. The radial decomposition of zircon starts from the surface to the centre of the grain, which leads to rapid crystallization of zirconia and to the formation of amorphous silica ^[8]. The presence of a glassy phase at some of the triple junctions will initiate at high temperatures, which is responsible for the decrease of strength of zircon at high temperature ^{[6][9]}.

In practice mullite-zirconia composites are employed in the glass industry and where a high chemical and corrosion stabilities are required. Zircon and alumina are largely employed as raw materials in their manufacture.

CHAPTER 2

LITERATURE REVIEW

2.1 Effect of additives on the properties of mullite-zirconia composites

Manas K.Haldar, T.K.Pal and G.Banerjee (Ceramics International 28 (2002) 311–318) observed that the addition of yttrium oxide overall improves the physical, thermo-mechanical properties of the composites. Here mullite–zirconia composites with 2–6 mol% yttrium oxide have been prepared from Indian coastal sillimanite beach sand, zirconia and alumina. Yttrium oxide helped in the grain growth of the samples. It was observed that the exaggerated grain growth is also responsible for higher porosity as the temperature increases but the composites with no yttrium oxide show downtrend in porosity with rise in temperature ⁽¹⁰⁾.

J. S. Moya, P. Miranzo and M. I. Osendi (Materials Science and Engineering, AI09 (1989) 139-145) demonstrated that the microstructure of mullite-zirconia and alumina- zirconia composites can be modified by additives. It was observed that the additives like CaO and MgO, that do not form a solid solution with the matrix encourage the sintering rate by a transitory liquid formation while TiO₂ additive that has a considerable solubility in the matrix affects the densification either by the creation of defects or by the formation of a transitory liquid phase, depending on the amount of addition. It was shown that the addition of TiO₂ results in an important effect on the mechanical properties of the composites because it is the controlling parameter for the zirconia grain growth ⁽¹¹⁾.

T. Ebadzadeh, E. Ghasemi (Ceramics International 28 (2002) 447–450) prepared mullite–zirconia composites by reaction sintering of α -alumina and aluminium nitrate as alumina sources,

and zircon powder. Results indicated that the addition of TiO_2 to mullite- ZrO_2 composites prepared from different alumina sources leads to change of reaction sintering, densification and microstructure which can alternately alter the formation temperature and retention of t- ZrO_2 phase in these composites. The tetragonal phase was not detected in the mixture of α -alumina and zircon sintered below 1500°C , while by adding TiO_2 due to the extent of reaction t- ZrO_2 peaks appeared at low sintering temperature (e.g. 1400°C).

At all sintering temperatures the composites derived from aluminium nitrate as the alumina source have higher t- ZrO_2 concentrations than when alumina was used (with and without TiO_2). The concentration of t- ZrO_2 decreased by introducing TiO_2 in aluminium nitrate derived composites ⁽¹²⁾.

Manas Kamal Haldar(Ceramics International 29 (2003) 573–581)prepared zirconia – mullite composites with 4-8mol% magnesium oxide from Indian coastal sillimanite beach sand, zirconia and alumina in the temperature range of $1500\text{--}1600^\circ\text{C}$. The X-ray diffraction showed all raw materials to be crystalline in nature. The bulk density of the sintered samples decreased with increase in temperature with varying amount of magnesia. The linear shrinkage of the sintered samples increased with higher content of magnesia. The sintered materials showed higher value of fracture toughness than pure mullite ⁽¹³⁾.

S. Maitra, S. Pal, S. Nath, A. Pandey, R. Lodha (Ceramics International 28 (2002) 819–826) synthesized precursor powder for zirconia–mullite composite by co-precipitation in aqueous medium taking inorganic salts of aluminium, silicon and zirconium in requisite amount and studied the role of two additives, namely, MgO and Cr_2O_3 , on the densification of the compacted

powder at different elevated temperatures ca. 1300–1500°C. It was observed that the batch containing only MgO as an additive showed a progressive and steady increase in bulk density and specific gravity while the batch containing both MgO and Cr₂O₃ as sintering aid contained more glassy phase compared to the batch containing only MgO. Mechanical properties like compressive strength, flexural strength and fracture toughness of the batch containing both MgO and Cr₂O₃ was also found to be better than the others. Probably Cr⁺³ doped expanded mullite crystals containing better interlocking matrix with reinforcement from t and m- ZrO₂, and MgO-containing liquid phase is a reason for this. All the batches contained mullite, corundum, cristobalite, tetragonal, monoclinic and cubic zirconia and some amount of glassy phase ⁽¹⁴⁾.

2.2 Objective of the present study

To observe the effect of TiO₂ addition on the phase formation and densification behaviour of Zirconia- Mullite composites.

CHAPTER 3

EXPERIMENTAL PROCEDURE

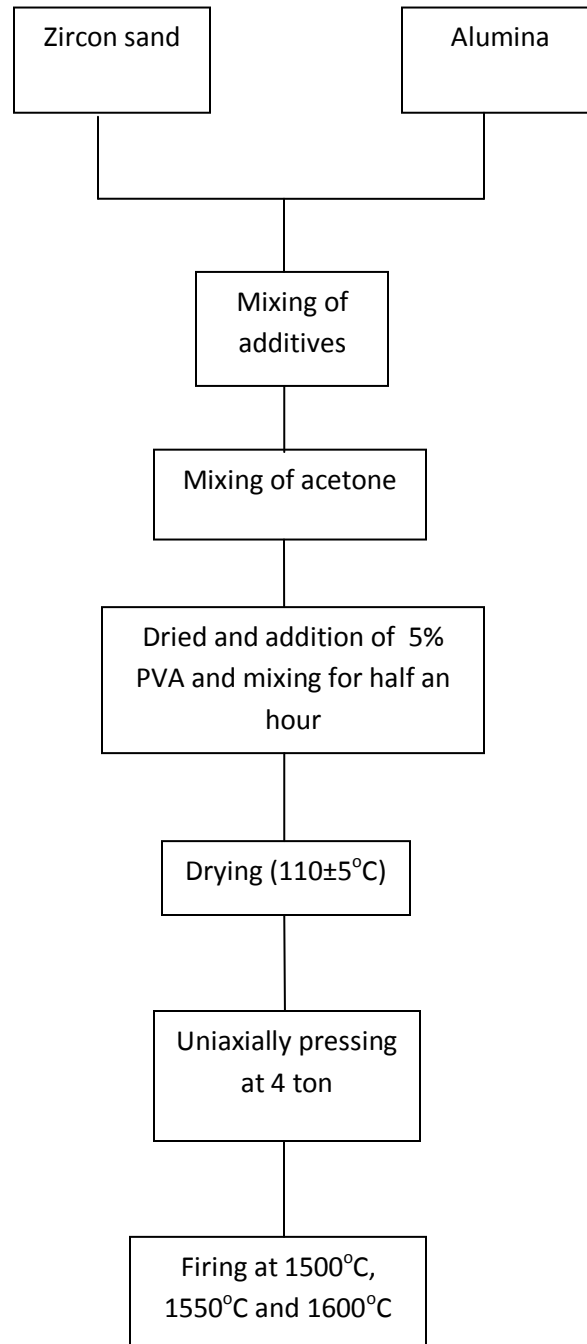
3.1 Procedure

Zircon sand and Alumina are used as major raw materials in the present studies. We have made four batches of different compositions: batch1 with no additive (ZMO), batch 2 with 0.1wt% additive (ZM1), batch 3 with 0.2wt% additive (ZM2) and batch 4 with 0.3wt% additive (ZM3). Both the raw materials are mixed with additive, TiO_2 in agate motor in required quantities. Acetone was added to different batches for homogenization and mixed for an hour. The mixture is then dried. After drying, each composition was mixed with 3% PVA, an organic binder for half an hour. Compositions obtained were dried at about $110 \pm 5^\circ\text{C}$ for 15-20minutes. They are then cooled at room temperatures and were crushed to break the agglomerates to fine powder and were uniaxially pressed at 4 ton to form briquettes. After drying the green samples were fired at 1500°C , 1550°C and 1600°C with 4hrs soaking time in an electric furnace.

Firing was done in an electric furnace and initially 650°C was achieved in an hour with 30 minutes of hold and then the heating rate was 3°C min^{-1} up to the final temperature. Fired products thus obtained were cooled to room temperature and characterized in terms of bulk density and apparent porosity. Shrinkage and bi-axial flexural strength of fired products were calculated. Phase analysis was done by XRD.

Bulk density and apparent porosity of the sintered product were measured by a conventional liquid displacement method using Archimedes Principle in water medium.

PROCESS FLOW SHEET



3.2 General characterization

Bulk Density

Bulk density of the sintered products was measured using conventional liquid displacement method using Archimedes Principle in water medium. Dry weight of the sintered samples was determined (W_d) and then they were kept in the boiling water for about 2 hrs to ensure complete filling of the open pores of the sintered samples. The temperature of the samples was then cooled down to room temperature and weight of the sample, suspended in water, was taken (W_{sus}). After that the weight of the sample in a fully soaked condition in air was taken (W_{soa}).

Bulk density and apparent porosity are measured using the following formulae:

$$\text{Bulk density } (D_b) = W_d / (W_{soa} - W_{sus})$$

$$\text{Apparent porosity (\%)} = (W_{soa} - W_d) / (W_{soa} - W_{sus}) * 100$$

Change in linear dimensions

For calculating change in linear dimensions, diameters of the sintered products were taken using digital vernier calipers. It was calculated using the formula:

$$\% \text{ Change in linear dimensions} = (G_{dia} - S_{dia}) / G_{dia}$$

where, G_{dia} = diameter of the green sample

S_{dia} = diameter of the sintered samples

Bi-axial flexural strength

Bi- axial flexural strengths of the samples sintered at different temperatures were measured. It is the capacity of a material to withstand axially directed pushing forces. When the limit of compressive strength is reached, materials are crushed. The apparatus used for calculating biaxial flexural strength applies a uniaxial compressive load.

Bi- axial flexural strength can be calculated by the formula: $2P / \pi DT$

where P = load applied

D = diameter of the sample

T = thickness of the sample

X-Ray Diffraction

The phase analysis of the sintered samples was done by Philips X-Ray Diffractometer PW 1730 with nickel filtered Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 30mA. Samples were scanned in a continuous mode from 20°-80° with a scanning rate of 0.04°sec⁻¹.

RESULTS AND DISCUSSIONS

4.1 Densification Study:

Densification is a very important step in ceramic forming process. Variation of bulk density of ZM0, ZM1, ZM2 & ZM3 with different sintering temperatures has been shown in Fig.1 and the results are tabulated in Table 1.

Table 1: Bulk density of sintered sample at different temperatures

Sample code	Sintering temperature		
	1500°C	1550°C	1600°C
ZM0	3.063	2.912	2.892
ZM1	3.027	2.887	3.149
ZM2	2.804	2.792	3.254
ZM3	2.559	2.711	2.962

Variation in bulk density can be seen with varying percentage of TiO_2 at different sintering temperatures. The highest density is achieved by ZM2 at 1600°C but it sharply decreases with further increase in additive. In ZM0, density has decreased with increase in sintering temperature while in ZM1 & ZM2 bulk density has decreased initially but then there is a steep increase in density at 1600°C. Densification here is due to the formation of a minor transient liquid phase i.e. ZrSiO_4 .

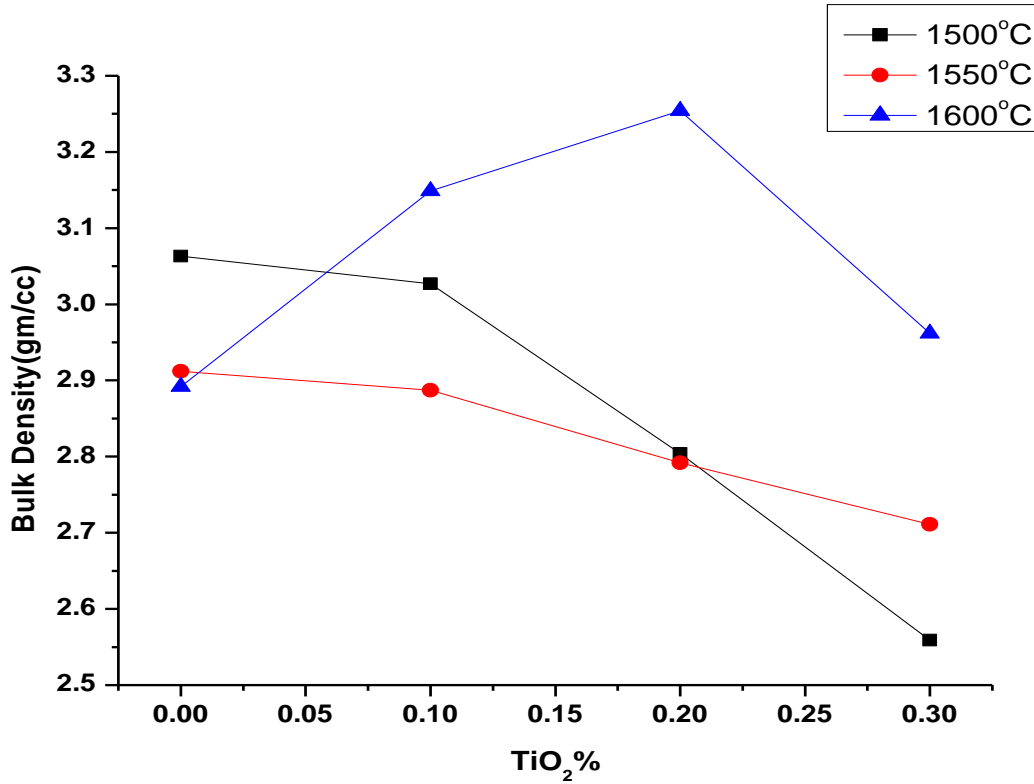


Fig.1: Variation in bulk density of zirconia-mullite composites with and without additives at different sintering temperature

Variation of apparent porosity of ZM0, ZM1, ZM2 & ZM3 with sintering temperatures has been shown in Fig. 2 and the results are given in Table 2. Apparent Porosity (A.P) initially decreases with temperature in all the three compositions whereas the decrease is more prominent in ZM1 & ZM2 in comparison to ZM0 and ZM3 from 1500°C - 1600°C. We can see that A.P values approach zero for the sample with 0.2wt% TiO₂ additive at 1600°C, the value is zero denoting a fully sintered phase; however there may be some amount closed pores. To be sure of the exact temperature of completion of sintering we have to carry out further firing between the two temperatures of 1550°C and 1650°C.

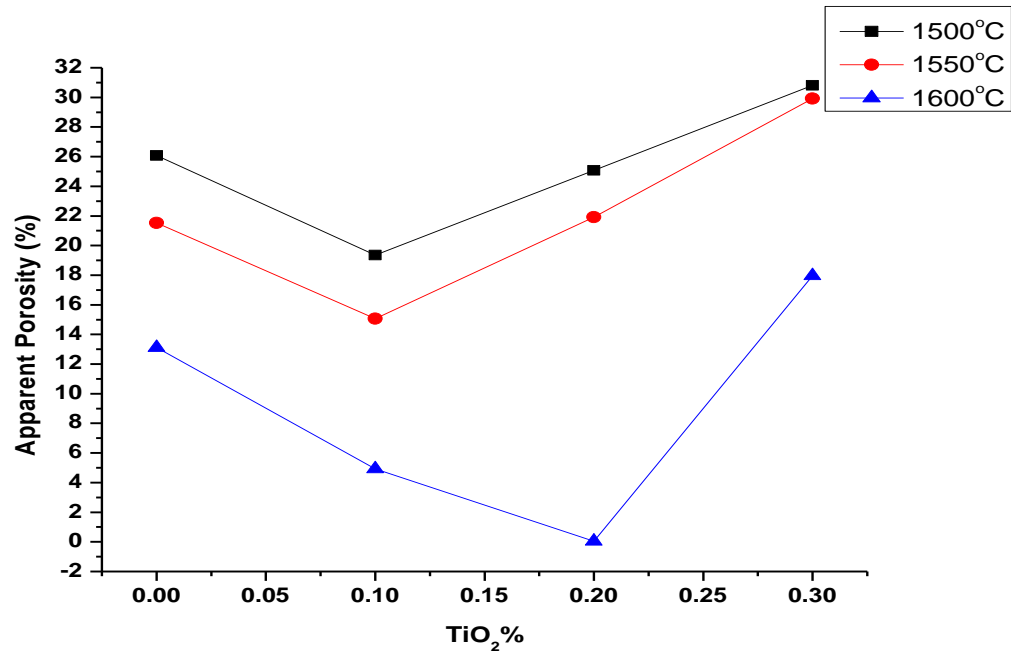


Fig.2: Variation in apparent porosity of sample with and without additive with sintering temperature

Table 2: Apparent porosity of sintered sample at different temperatures

sample code	Temperature		
	1500°C	1550°C	1600°C
ZM0	26.07	21.53	13.12
ZM1	19.36	15.06	4.92
ZM2	25.08	21.92	0.05
ZM3	30.81	29.92	17.96

4.2 Change in linear dimensions

Diameters of the sintered samples were calculated using vernier calipers. Variations in the dimensions of the sintered samples at temperatures 1500°C, 1550°C & 1600°C are tabulated in Table 3, Table 4 & Table 5 respectively.

Table 3. Percentage change in linear dimensions of the samples sintered at 1500°C

sample code	Diameters	% change in linear dimensions
ZMO	12.05	-0.02
ZM1	11.87	1.33
ZM2	12.19	-1.33
ZM3	12.05	-0.02

Table 4. Percentage change in linear dimensions of the samples sintered at 1550°C

sample code	Diameters	% change in linear dimensions
ZMO	11.9	1.08
ZM1	11.78	2.08
ZM2	12.07	-0.003
ZM3	11.91	1.00

Table 5. Percentage change in linear dimensions of the samples sintered at 1600°C

sample code	Diameters	% change in linear dimensions
ZMO	11.42	5.07
ZM1	11.22	6.73
ZM2	11.40	5.24
ZM3	11.58	3.74

Table 3,4&5 and Fig.3; shows that at lower temperature the sample has undergone some expansion and very negligible shrinkage but with the increase in temperature it has increased. Large amount of shrinkage is achieved at 1600°C in samples containing 0.1 and 0.2% TiO_2 because addition of TiO_2 results in the formation of liquid phase thus causing densification and removal of pores but with further increase in the additive it has decreased considerably.

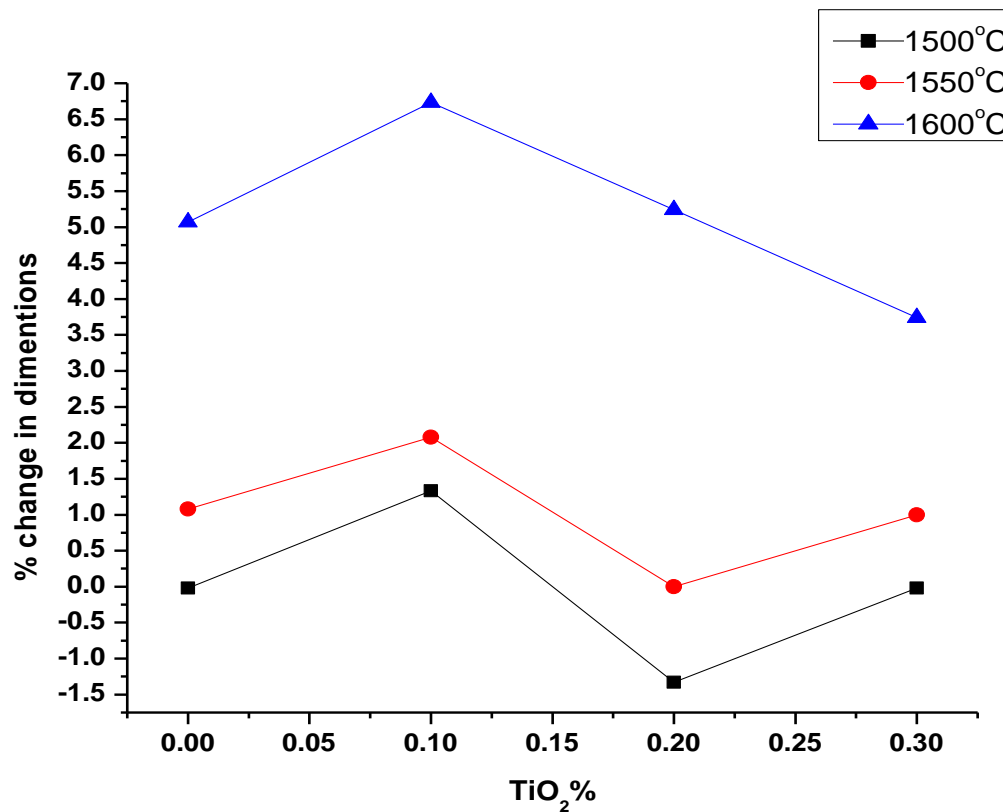


Fig.3 Variation in the dimensions of the sintered samples with the addition of TiO_2 at different temperatures

4.3 Biaxial flexural strength

Diameters and thickness of the sintered samples were calculated and biaxial flexural strength was measured. Biaxial flexural strengths of the samples with different amounts of additives at different sintering temperatures are tabulated in Table 6 and shown in fig. 4.

Table 6. Biaxial flexural strengths of the sintered samples at different temperatures

Sample Code ↓ Temperature →	Biaxial Flexural Strength(MPa)		
	1500°C	1550°C	1600°C
ZM0	617	523	683
ZM1	497.6	770	1036
ZM2	460.9	452.9	883
ZM3	411	335.6	601

Table 6 and Fig. 4, shows that for each composition biaxial strength increases with increase in temperature. Steep increase can be seen in the strength from 1500°C to 1600°C. But increase in the addition of TiO₂ has resulted in decrease of biaxial flexural strength at temperature 1500°C and at 1550°C it has increased for samples scontaining 0.1% TiO₂ but again with further increase

it has reduced. While at higher temperature, 1600°C maximum biaxial flexural strength has been achieved by the composition containing 0.1% TiO_2 .

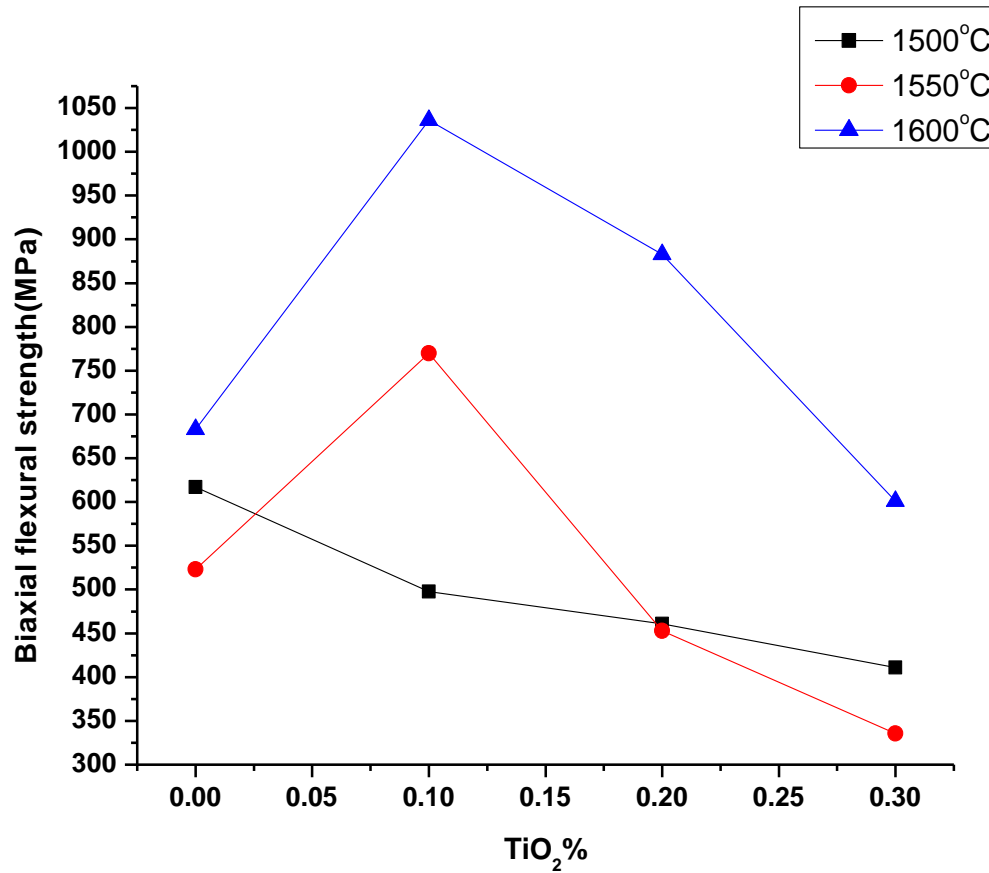


Fig.4 Variation in the biaxial flexural strengths with varying temperatures and additive

4.4 Phase Analysis

X-ray diffraction pattern of the sample sintered at 1500°C is shown in **Fig.5**

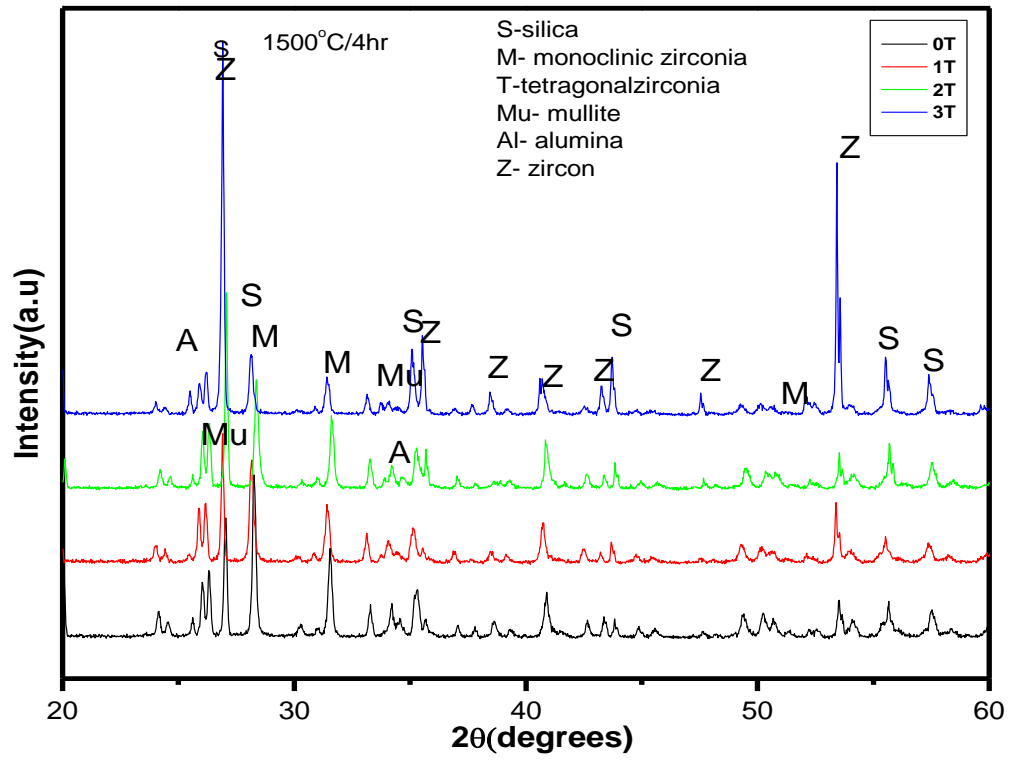


Fig.5 XRD of the sintered sample at 1500°C

X-ray diffraction pattern of the sample sintered at 1550°C is shown in **Fig.6**

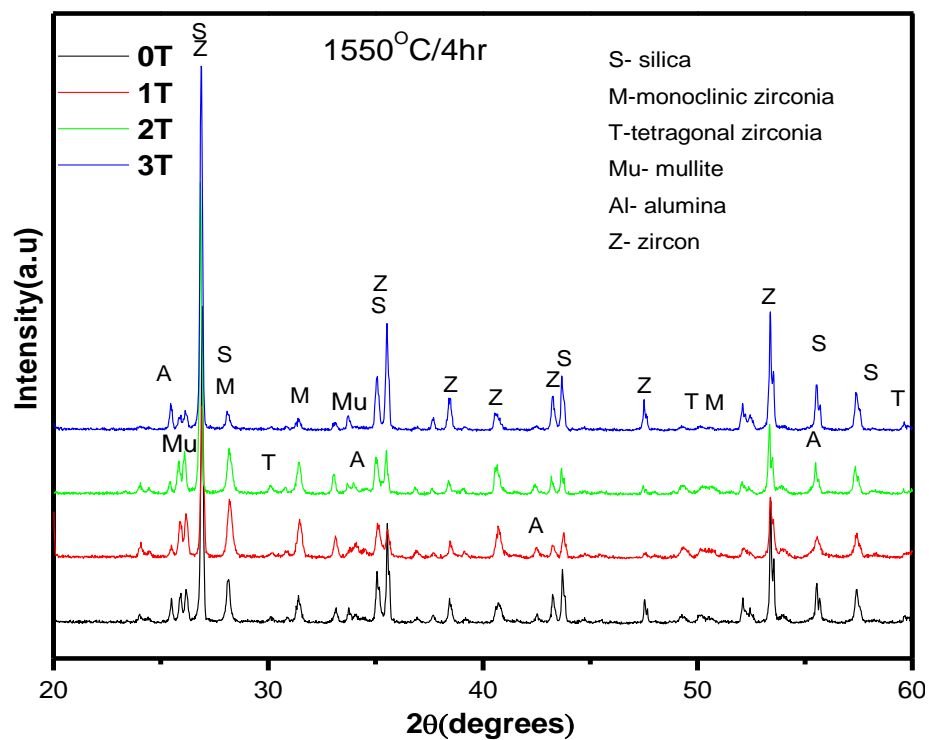


Fig.6 XRD of the sintered sample at 1550°C

X-ray diffraction pattern of the sample sintered at 1550°C is shown in **Fig.7**

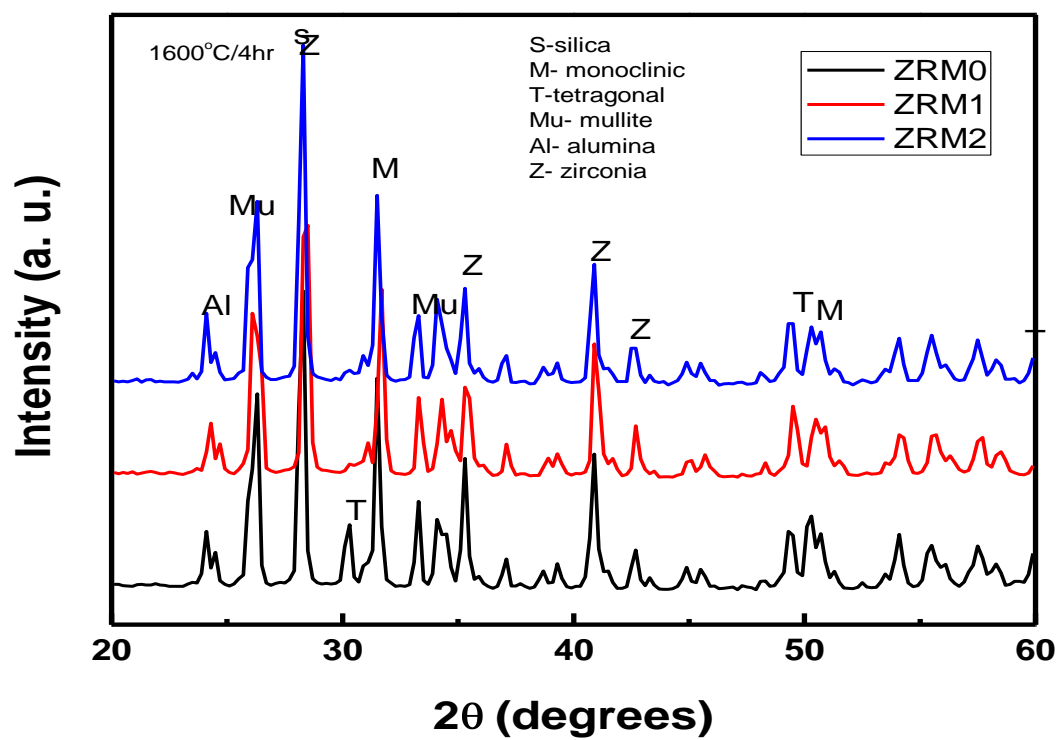


Fig.7 XRD of the sintered sample at 1600°C

CHAPTER 5

CONCLUSION

In the first part of our investigation, sintering of zircon sand and alumina mixture with and without additives was done at 1500°C, 1550°C and 1600°C. Characterization of the sintered products was done in terms of physical properties (e.g. Bulk density, apparent porosity), phase analysis by XRD, biaxial flexural strength and variation in dimensions. The densification study shows that the use of liquid phase forming additives in the composites causes densification at 1600°C with 0.2% TiO₂. This was confirmed by observing the apparent porosity and bulk density. Measurements of biaxial flexural strengths confirm that the maximum strength is obtained at 1600°C by the sample containing 0.2% TiO₂.

REFERENCES

- (1) Francois Cradarelli, Materials Handbook: A Concise Desktop Reference, 620-621.
- (2) A.J. Skoog, R.E. Moore, Refractory of the past for the future: mullite and its uses as a bonding phase, *Ceram. Bull.* **67** (7) (1988) 1180-1185.
- (3) H.S. Tripathi, G. Banerjee, Effect of chemical composition in sintering and properties of $\text{Al}_2\text{O}_3\text{-SiO}_2$ derived from sillimanite beach sand, *Ceram. Int.* **25**(1) (1999) 19-25.
- (4) H.S. Tripathi, S.K. Das, B. Mukherjee, A. Ghosh, G. Banerjee, Synthesis and thermo-mechanical properties of mullite- alumina composite derived from sillimanite beach sand: effect of ZrO_2 , *Ceram. Int.* **27**(8) (2001) 833- 837.
- (5) B.O. Mysen, Phase Diagrams for Ceramists, National Institute of Standards and Technology, *The American Ceramic Soc.* **8** (1990) 188.
- (6) Y. Shi, X.X. Huang, D.S. Yen, Fabrication of hot-pressed zircon ceramics: mechanical properties and microstructure, *Ceram. Int.* **23** (5) (1997) 457–462.
- (7) S. Lathabai, D.G. Hay, F. Wagner, N. Claussen, Reaction-bonded mullite/zirconia composites, *J. Am. Ceram. Soc.* **79** (1) (1996) 248–256.
- (8) F. Cambier, C.B. Delastra, P. Pilate, A. Leriche, Formation of microstructural defects in mullite–zirconia and mullite–alumina– zirconia composites obtained by reaction-sintering of mixed powders, *Trans. J. Br. Ceram. Soc.* **83** (6) (1984) 196–200.
- (9) Cemal Aksel, Mechanical properties and thermal shock behaviour of alumina-mullite-zirconia and alumina-mullite refractory materials by slip casting, *Ceramics International*, **29** (2003) 311-316.

- (10) Manas K.Haldar, T.K.Pal and G.Banerjee, Preparation and properties of Y_2O_3 containing zirconia–mullite composites derived from sillimanite beach sand, *Ceramics International*, **28** (2002) 311–318.
- (11) J.S. Moya, P.Miranzo and M.I. Osendi, Influence of additives on the microstructural development of mullite- ZrO_2 and alumina- ZrO_2 , *Materials Science and Engineering*, **AI09**(1989)139-145.
- (12) T. Ebadzadeh, E. Ghasemi, Effect of TiO_2 addition on the stability of t- ZrO_2 in mullite– ZrO_2 composites prepared from various starting materials, *Ceramics International*, **28** (2002) 447–450.
- (13) Manas Kamal Haldar, Effect of magnesia additions on the properties of zirconia–mullite composites derived from sillimanite beach sand, *Ceramics International*, **29** (2003) 573–581.
- (14) S. Maitra, S. Pal, S. Nath, A. Pandey, R. Lodha, Role of MgO and Cr_2O_3 additives on the properties of zirconia–mullite composites, *Ceramics International*, **28** (2002) 819–826.